

Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed

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Abstract Combustion of fossil fuels is one of the major sources of greenhouse gas (GHG) CO₂, it is therefore necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of GHG. Removal of CO₂ from flue gasses has become an effective way to mitigate the GHG and adsorption is considered to be one of the methods. Adsorption of CO₂ on zeolite 13X, zeolite 4A and activated carbon (AC) have been investigated at a temperature ranging from 25 to 60 °C and pressure up to 1 bar. The experimental data were fitted with isotherm models like Langmuir and Freunlich isotherm model. The Langmuir model fit well with the two zeolites and Freunlich model fit well with AC. The thermodynamics parameters were calculated and found to be exothermic in natures for all three adsorbents. Moreover, regeneration studies have been conducted in order to verify the possibility of activated carbon reutilization, to determine its CO₂ adsorption capacity within consecutive cycles of adsorption–desorption. Temperature swing adsorption was employed as the regeneration method through heating up to a temperature of approximately 100 °C. There is no full reversibility for zeolites while AC can achieve complete regenerations.

Keywords Adsorption · Carbon dioxide · Thermodynamic parameters · Activated carbon · Zeolite

Introduction

The emission of gaseous products of combustion into the atmosphere, mainly Carbon dioxide (CO₂) is regarded as a major cause of global warming and climate change, through the so-called greenhouse effect [1]. Currently, 85 % of total world demanded energy is supplied by thermal power plants fed by fossil fuels, including coal, oil and gas. They account for about 40 % of total CO₂ emissions [2]; Yang et al. [3]; [4]. Among the ways to control, reduce or mitigate this effect, the capture of CO₂ from flue gasses of industrial combustion processes and its storage in deep geological formations is now being considered as a serious option [5–7].

A number of adsorption processes are used commercially for adsorbent process, including pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA), and thermal or temperature swing adsorption (TSA). A number of research works have been done using the processes mentioned above on different types of adsorbent materials. Recent developments have demonstrated that PSA is a promising option for separating CO₂ due to its ease of applicability over a relatively wide range of temperature and pressure conditions, its low energy requirements, and its low capital investment cost (Agarwal et al. [8]). Many studies concerning CO₂ removal from various flue gas mixtures by means of PSA processes have been addressed in the literature. Prior to the design of an adsorption process, selecting an appropriate adsorbent with high selectivity and working capacity, as well as a strong desorption capability, is key to separating CO₂. As a result, a wide variety of adsorbents like activated carbon, zeolites, silica gel, activated alumina, urea–formaldehyde and melamine–formaldehyde resins, poly-ethyleneimine and hollow fiber carbon membranes based adsorbents, etc. have

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been investigated for this purpose [9]; Sircar et al. [10]; [11, 12, 17]. Recent development shows an improvement in adsorbent materials with higher adsorption capacity and selectivity like Activated carbon honeycomb monolith—Zeolite 13X hybrid system, zeolites NaKA and nano-NaKA, FAU zeolites and zeolite 13X prepared from bentonite [13–16].

The PSA process is based on preferential adsorption of the desired gas on a porous adsorbent at high pressure, and recovery of the gas at low pressure. Thus, the porous sorbent can be reused for subsequent adsorption. PSA technology has gained interest because of the low energy requirements and low capital investment costs. The low recovery rate of CO₂ is one of the problems reported with the PSA process [18]. Development of regenerable sorbents that have high selectivity, adsorption capacity, and adsorption/desorption rates for CO₂ capture is critical for the success of the PSA process. Cost of the sorbent is also a major factor that needs to be considered for the process to be economical [19, 20].

The adsorption method of choice for many zeolite molecular sieves is PSA, although some experiments have employed a combined pressure and temperature swing adsorption (PTSA) process (Ruthven et al. [21]; [22, 23]. It has been reported that a particular TSA and PSA cycle conditions would result in higher expected working capacity with an increase in feed temperature. Zeolites have shown promising results for the separation of CO₂ from gas mixtures and can potentially be used for the PSA process. Natural zeolites are inexpensive and can be viable sorbents if they work for the process application [24]. It has also been reported that using AC as an adsorbent material, the adsorption capacity can increase till 30 Bar and become steady after 30–35 bars [25].

Based on the literatures available, PSA seems to be the best option for separating CO₂ from flue gas due to its ease of applicability over a relatively wide range of temperature and pressure conditions. A number of sorbents like zeolite, activated alumina, activated carbons, etc. have been utilized and cost of the sorbents play a vital role for the process to be economical. In this paper, low cost and abundantly available locally, coconut fiber based AC was employed as the sorbent materials and compared with commercial zeolites. Work had been done to develop a process in which CO₂ was adsorbed from a gas stream containing ~13.8 vol. % of CO₂ onto zeolite 13X, zeolite 4A and AC by means of PSA process. The system was tested for five different adsorption and desorption cycles in order to determine the adsorbent bed's regeneration efficiencies. Kinetics and adsorption thermodynamics parameters have also been calculated.

Materials and methods

Materials

The properties of commercial zeolite 13X and Zeolite 4A which were purchased from the local chemist are given in Table 1. While the AC (coconut fiber) used was obtained from a local area. It was peeled and the fibrous part was collected and was broken into small pieces. The coconut fibre was washed with water, dried in the sun for 10 h and transferred to the furnace. The coconut pieces were burnt distinctively in the furnace for an hour at a temperature of 350 °C. The charcoal produced was withdrawn from the furnace and sieved; a mean particle diameter of 0.92 mm was obtained. The material characterization was done for proximate and ultimate analysis and details of the physical and chemical properties are given in Table 2.

Table 1 Properties of zeolites

| Properties | 4A | 13X |
|--------------------------------------|------|------|
| BET surface area (m ² /g) | 434 | 720 |
| Pore diameter (Å) | 4.0 | 10.0 |
| Bulk density (kg/m ³) | 700 | 639 |
| Particles diameter (mm) | 1.5 | 2 |
| Composition (wt %) | | |
| Sodium | 10.8 | 11.9 |
| Aluminum | 13.6 | 14.3 |
| Silicon | 16.1 | 17.8 |
| Calcium | 0.8 | 0.6 |
| Potassium | 0.9 | 0.2 |
| Magnesium | 1.2 | 1.3 |

Table 2 Properties of activated carbon

| | | | |
|--------------------------------------|----------|--------------|----------|
| BET surface area (m ² /g) | 214 | | |
| Pore volume (cc/g) | 0.068 | | |
| Bulk density (kg/m ³) | 350 | | |
| Particles diameter (mm) | 0.92 | | |
| Ultimate analysis (wt %) | | | |
| C | O | Cl | K |
| 41.28 | 36.00 | 6.01 | 33.71 |
| Proximate analysis (wt %) | | | |
| Ash | Moisture | Fixed carbon | Volatile |
| 4.8 | 10.63 | 14.49 | 70.08 |



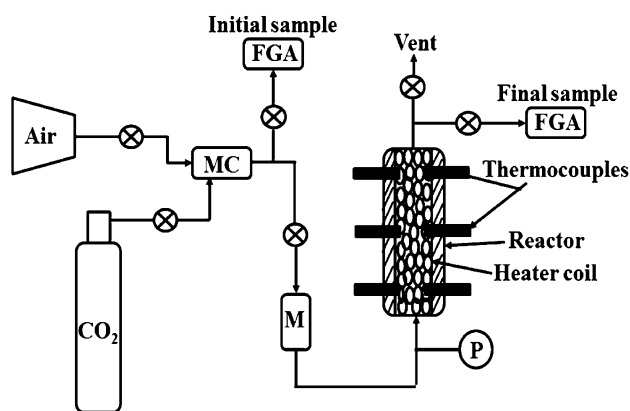


Fig. 1 Schematic of the experimental set-up for fixed bed. *MC* mixing chamber, *M* mass flow meter, *P* pressure gage, *FGA* flue gas analyzer

Table 3 Experimental conditions

| | |
|--|-------------|
| Bed weight | 20 g |
| Reactor length | 200 mm |
| Reactor diameter | 30 mm |
| Influent CO ₂ concentration | 13.8 vol. % |
| Inlet flow rate | 15 LPM |
| Bed porosity | 0.5 |
| Superficial velocity | 0.13 m/s |
| Adsorption temperature | 25–60 °C |
| Adsorption total pressure | 1 bar |

Methods

The experimental set-up for the adsorption test consists of a CO₂ cylinder and Gas Compressor interconnected through a pipe to the system as shown in Fig. 1 based on [25]. The Gas Compressor could provide sufficient pressure up to 10 kg/cm² with a discharge capacity of 84 LPM. The gas mixing chamber was made up of a GI pipe of 20 mm diameter and 80 mm in length to achieve the required mixture of air and CO₂ (13.8 vol. %) at a constant rate. Ceramic wool was wrapped around the reactor above the heater coil for insulation. Thermocouples (K-type) were inserted in the bed to measure the bed temperatures with accuracy of ±0.5 %.

A Glass Tube Rotameter of the range 0–35 LPM was used to control the mass flow rate and measure the mass flow rate of the incoming gas. The reactor was made up of GI pipe with 30 mm diameter with 1.5 mm wall thickness and 200 mm in height. A pressure monitoring system was attached to know the incoming pressure and experiments were carried at varying pressure to see the effect of pressure in the adsorption process at a constant temperature. A number of needle valves were attached in the system to control the system operation at

the require rate. Flue Gas Analyzer (KM9106) was used to measure the inlet sample gas and the outlet gas properties. The apparatus was tested for leak absence and for accuracy through calibrations with an empty tank. Table 3 give details of the operating parameters.

The process employed a single-bed PSA unit. For the adsorption process, first the air was allowed to flow through the reactor and then followed by carbon dioxide. To maintain equal flow rate and pressure of both the flows, the gas mixture was allowed to pass through the mixing chamber. The flow of air was then stopped and allowed only the pure CO₂ to flow through the reactor for measurement of the mass of CO₂ adsorbed per the mass of the adsorbent. To know the effective adsorbed mass on the adsorbent materials, Q_{eff} , two quantities were defined: Q_t that is the mass containing the reactor including the adsorbents and Q_d which is the mass of the empty reactor or dead volume. The Q_{eff} was then calculated with the equation as follows: $Q_{\text{eff}} = Q_t - Q_d$.

Results and discussions

Adsorption breakthrough curves

Adsorption is a transient process and the amounts of material adsorbed within a bed depend both on position and time. The CO₂ breakthrough curves for the three adsorbents are shown through Figs. 2, 3, 4 and the experimental conditions are given in Table 3. The breakthrough curves show ratio of the outlet concentration and the influent concentration against the contact time at an atmospheric pressure, and at a temperatures of 25, 35, 45 and 60 °C. The general pattern of the breakthrough curves were achieved as expected for all adsorbents. For zeolite 13X, the adsorption breakthrough occurs at 20 min and for zeolite 4A, the adsorption breakthrough occurs at 16 min.

This shows that the pore diameter of zeolite 13X (10 Å) and zeolite 4A (4 Å) is sufficient for the CO₂ to enter into the zeolites channels. The major cations of zeolites are Na and K and this major cation appears to play a main role in the adsorption of CO₂. Also, sodium appears to be the favorable cation for the adsorption of CO₂. The saturation time for zeolite 13X is longer than that of zeolite 4A which is due to the larger pore volume. For AC, the breakthrough time is 8 min at 25 °C. The breakthrough time with AC was shorter as compared to zeolites, indicating that the CO₂ adsorption capacity of AC is lower than that of zeolites. The differences in adsorption observed with zeolites and AC should be related to the differences in the chemical nature at the surface and porosity. Both the zeolites have higher surface area than AC and that may have contributed to the higher adsorption capacity of zeolites.



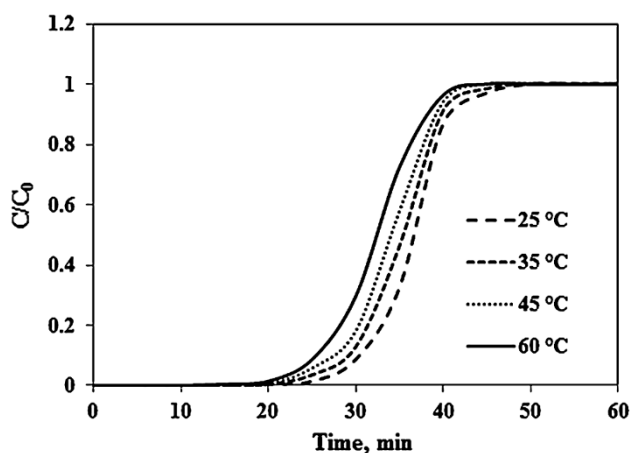


Fig. 2 CO₂ breakthrough curve for zeolite 13X at 1 bar

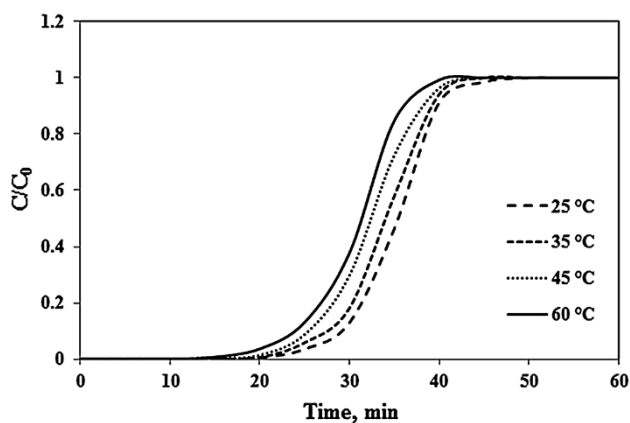


Fig. 3 CO₂ breakthrough curve for zeolite 4A at 1 bar

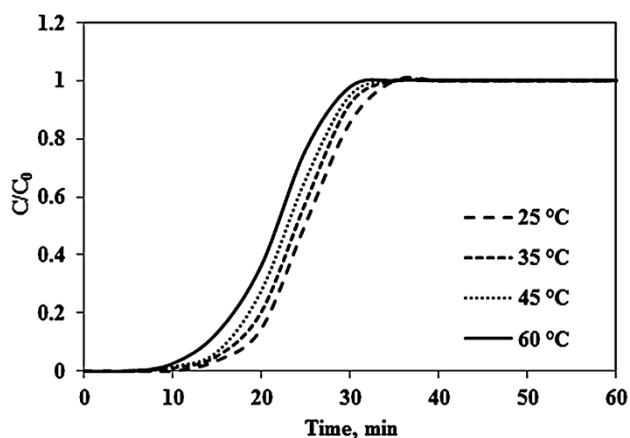


Fig. 4 CO₂ breakthrough curve for AC at 1 bar

Adsorption isotherms

In this study, the CO₂ adsorption for each adsorbent was measured under a series of isothermal conditions (i.e., 25,

35, 45 and 60 °C). It can be seen that all isotherm curves exhibit common behavior regardless of temperature and adsorbent type which mean the amount of CO₂ adsorbed on the adsorbent increases very rapidly with the increase in pressure over the low pressure range, and it tends to stabilize as the pressure continues to increase as shown in Figs. 5, 6 and 7. The isotherms behavior follows the type-I isotherm category according to IUPAC adsorption isotherm classification [26], which indicates a monolayer adsorption mechanism, commonly applied to micro-porous adsorbents.

The adsorption isotherms curves reveal the typical behavior showing the effect of temperature on the CO₂ adsorption capacity. That is, an increase in adsorption temperature leads to a reduction in the amount of adsorbed CO₂. Rising temperature simply provides more internal energy to CO₂ molecules in the gas phase. It should be noted that the increasing energy allows gaseous molecules to diffuse at a greater rate, but, at the same time, it reduces the chance for the CO₂ to be restrained or trapped by fixed energy adsorption sites on the adsorbent surface.

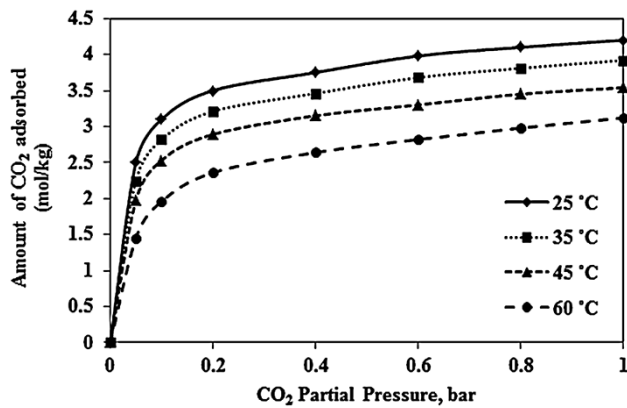
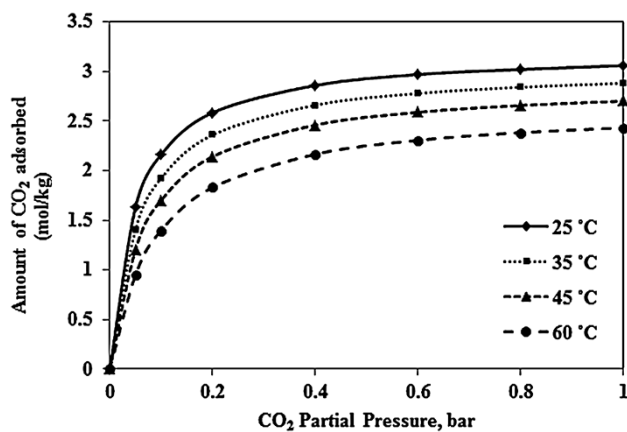
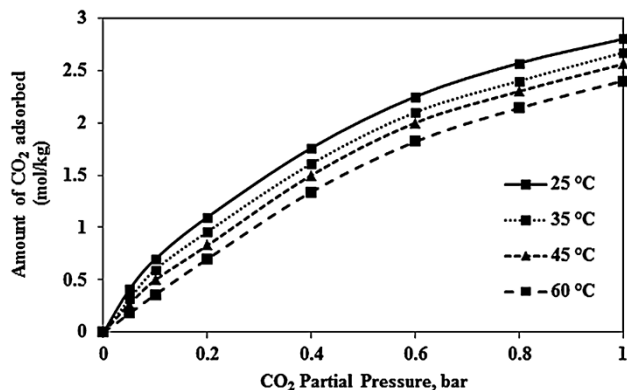
The amount of CO₂ adsorbed by using zeolite 13X is 4.215 mol_{CO₂} kg_{sorbent}⁻¹ while the amount of CO₂ adsorbed by using zeolite 4A is 3.263 mol_{CO₂} kg_{sorbent}⁻¹ at 1 bar and a temperature of 25 °C. AC gives the lowest adsorption capacity with an amount of 2.828 mol_{CO₂} kg_{sorbent}⁻¹ for this particular study. At higher temperature, CO₂ adsorption capacity for the adsorbents decreases by 20–30 %. In addition, the slope of adsorption isotherm curve reveals the strength of interaction between CO₂ molecules and the adsorption sites for individual sorbents. It appears that zeolite based adsorbents which exhibit greater slope of the adsorption curves have stronger adsorption sites as compare to AC. The experimental data were fitted to standard isotherm models like Langmuir and Freundlich model. The Langmuir isotherm equation can be represented as shown in Eq. 1 [27]

$$q = \frac{q_m K P_{CO_2}}{1 + K P_{CO_2}} \quad (1)$$

where q is the amount of CO₂ adsorbed at the CO₂ partial pressure P and q_m is the amount of CO₂ adsorbed with monolayer coverage. The values of q_m and Langmuir constant K , calculated from the CO₂ adsorption isotherms, are listed in Table 4. The monolayer CO₂ coverage at the different temperatures 25, 35, 45 and 60 °C were well-fitted for the zeolite adsorbents. While, Freundlich equation takes the form as shown in Eq. 2 [27]:

$$q = K P_{CO_2}^{1/n} \quad (2)$$

where K and n are Freundlich model constants. The K and n values of zeolite are higher than that of activated carbon. The Freundlich constant and regression co-efficient are given in Table 5 and agree well with AC.

Fig. 5 CO₂ adsorption isotherms on zeolite 13XFig. 6 CO₂ adsorption isotherms on zeolite 4AFig. 7 CO₂ adsorption isotherm on AC

The average percent deviation quantity, Δq , or the adsorbed amounts were calculated using the following formula given in Eq. 3 [28]:

Table 4 Langmuir constants and their regression coefficient

| Material | Temp (°C) | Langmuir constant | | R^2 | Δq % |
|-------------|-----------|-------------------|--------|-------|--------------|
| | | q_m | K | | |
| Zeolite 13X | 25 | 4.245 | 19.031 | 0.987 | 6.6 |
| | 35 | 3.971 | 16.875 | 0.978 | 9.7 |
| | 45 | 3.521 | 13.747 | 0.987 | 8.5 |
| | 60 | 3.173 | 11.202 | 0.978 | 10.8 |
| Zeolite 4A | 25 | 3.263 | 19.031 | 0.997 | 5.4 |
| | 35 | 3.071 | 16.875 | 0.974 | 12.5 |
| | 45 | 2.921 | 13.747 | 0.979 | 7.9 |
| | 60 | 2.617 | 11.202 | 0.989 | 9.5 |
| AC | 25 | 2.828 | 21.956 | 0.961 | 9.8 |
| | 35 | 2.711 | 19.119 | 0.933 | 8.5 |
| | 45 | 2.591 | 15.502 | 0.948 | 12.7 |
| | 60 | 2.494 | 11.759 | 0.939 | 10.5 |

Table 5 Freunlich constants and their regression coefficients

| Material | Temp (°C) | Freunlich constant | | R^2 | Δq % |
|-------------|-----------|--------------------|-------|-------|--------------|
| | | K | n | | |
| Zeolite 13X | 25 | 1.122 | 6.127 | 0.918 | 6.7 |
| | 35 | 1.034 | 5.483 | 0.938 | 10.5 |
| | 45 | 0.952 | 4.594 | 0.925 | 9.5 |
| | 60 | 0.836 | 3.812 | 0.973 | 12.3 |
| Zeolite 4A | 25 | 1.122 | 5.025 | 0.917 | 9.5 |
| | 35 | 1.034 | 4.386 | 0.923 | 11.2 |
| | 45 | 0.952 | 3.891 | 0.929 | 10.4 |
| | 60 | 0.836 | 3.311 | 0.937 | 9.7 |
| AC | 25 | 0.505 | 1.701 | 0.987 | 5.4 |
| | 35 | 0.447 | 1.551 | 0.982 | 8.4 |
| | 45 | 0.383 | 1.387 | 0.995 | 9.1 |
| | 60 | 0.346 | 1.319 | 0.986 | 6.7 |

$$\Delta q\% = \frac{100}{h} \sum_{j=1}^h \left| \frac{N^{\text{exp}} - N^{\text{cal}}}{N^{\text{exp}}} \right| \quad (3)$$

where h is the number of experimental data and N^{exp} and N^{cal} are the experimental and calculated number of moles that are adsorbed by the adsorbent pellet.

Adsorption thermodynamics

The thermodynamic parameters are calculated from the Langmuir isotherms by using the Vant'Hoff's equation as follows in Eq. 4–6 [29]:

$$\Delta G^\circ = -RT \ln K_l \quad (4)$$



Table 6 Thermodynamic parameters for the adsorption of CO₂

| Material | Temp (°C) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/mol.K) |
|-------------|-----------|---------------------------|---------------------------|----------------------------|
| Zeolite 13X | 25 | −7.929 | −11.274 | 17.568 |
| | 35 | −7.689 | | |
| | 45 | −6.299 | | |
| | 60 | −6.236 | | |
| Zeolite 4A | 25 | −7.299 | −12.852 | 18.499 |
| | 35 | −7.236 | | |
| | 45 | −6.929 | | |
| | 60 | −6.689 | | |
| AC | 25 | −7.653 | −14.98 | 24.379 |
| | 35 | −7.556 | | |
| | 45 | −7.247 | | |
| | 60 | −6.824 | | |

$$\Delta H^\circ = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1} \quad (5)$$

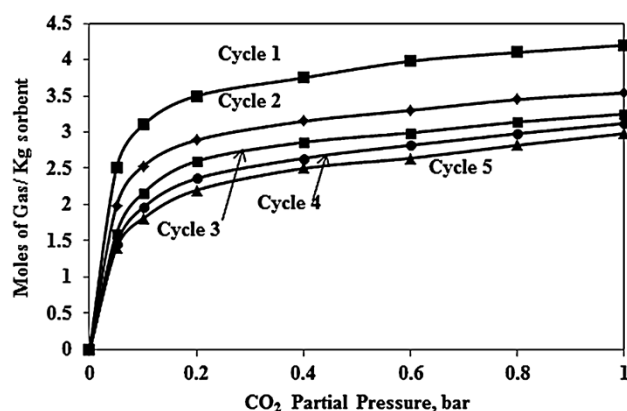
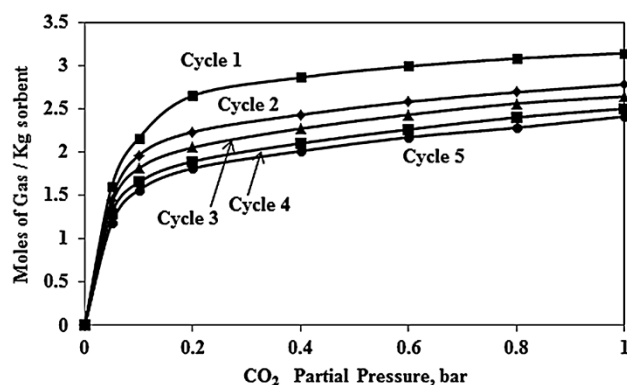
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (6)$$

where ΔG° is change in the Gibb's free energy, ΔH° is change in the enthalpy and ΔS° is change in the entropy. A plot of $\ln K_{eq}$ vs. $1/T$ should be a straight line with a slope = $-\Delta H^\circ/R$ and an intercept = $\Delta S^\circ/R$ which is called Van't Hoff equation.

The thermodynamic parameters, Gibbs free energy change, ΔG° was calculated using Langmuir constants and the results are listed in Table 6. The enthalpy change, ΔH° and the entropy change, ΔS° , for the CO₂ adsorption process on zeolite 13X are −11.274 kJ/mol and 17.568 J/mol.K respectively, while the enthalpy change and entropy change for zeolite 13X and zeolite 4A were calculated to give −12.852 kJ/mol and −18.499 J/mol.K respectively. For AC, enthalpy change, ΔH° and entropy change, ΔS° are −14.98 kJ/mol and −24.379 J/mol.K respectively. The negatives values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption process. The negative values in ΔH° indicated that the adsorption reaction is exothermic for all the adsorbents used. The positive value of ΔS° reflects the affinity of the adsorbents with CO₂ and suggests some structural change in CO₂ and the adsorbents.

Regeneration study

The three adsorbents were tested for material aging by using the same adsorbent over five adsorption desorption cycles at 25 °C and at 1 bar. The desorption process is achieved by increasing the bed temperature up to 100 °C which increases the internal energy of the gas and allowed the gas molecules to escape from the reactor. Figure 8

**Fig. 8** Adsorption isotherms of zeolite 13X**Fig. 9** Adsorption isotherms of zeolite 4A

shows the adsorption isotherms of CO₂ zeolite 13X at 25 °C for five cycles. Up to 0.2 bar the CO₂ adsorption increased rapidly when the pressure was increased. The increase in CO₂ adsorption after 0.2 bar appeared to be gradual. The adsorption isotherms for repeated cycles showed a reduction in the amount of adsorption for the next cycles. This indicated that the adsorption is not reversible and complete regeneration cannot be obtained by adsorption of the material after adsorption. The amount of adsorption is almost similar for cycles 4 and 5 which indicate that the adsorbent is almost saturated with CO₂ (Table 6).

The adsorption isotherms for zeolite 4A are shown in Fig. 9 and shows that the adsorption isotherms of CO₂ for zeolite 4A is not highly reproducible, indicating that the adsorption is not completely reversible. The adsorption at the first cycle was the highest. The uptake of CO₂ for molecular sieve 4A was lower than that of molecular sieve 13X at all pressures up to 1 bar. The adsorption isotherms for AC are shown in Fig. 10. It is interesting to note that all the isotherms are extremely reproducible, which indicates the excellent reversibility of adsorption. The CO₂ uptake for AC was lower than that of the two



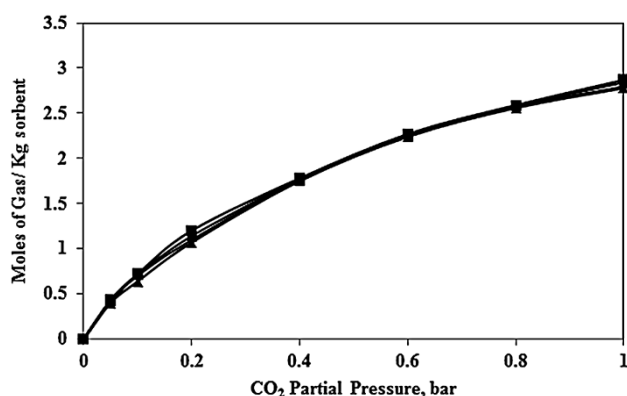


Fig. 10 Adsorption isotherms of AC

zeolite at lower pressures, but at higher pressures (up to 35 bar) the CO₂ uptake for AC was higher than that of the zeolites [25].

Conclusions

The CO₂ adsorption experiments were conducted using gravimetric method at different temperatures and pressures. From this study, it was concluded that the CO₂ adsorption isotherm obtained in this study followed general gas adsorption behavior, demonstrating that the CO₂ adsorption capacity increases with increasing pressure and decreases with increasing temperature. The adsorption isotherm follows a type-I isotherm classification according to IUPAC, representing a monolayer adsorption mechanism. Among the three adsorbents tested, zeolite 13X offers the highest adsorption capacity, and AC provides the lowest capacity at temperatures ranging from 25 to 60 °C and pressures up to 1 bar. The experimental data of CO₂ adsorption were fitted with Langmuir and Freundlich isotherm models. It was found that Langmuir model showed the best fit with the zeolite 13X and zeolite 4A while Freundlich model provided excellent fit with AC. The thermodynamics parameter were calculated from Van't Hoff's equation and concluded that the adsorption experiment were exothermic in nature for the three adsorbents. There is no full regeneration for zeolites while a full regeneration can be achieved with AC.

Authors' contributions All authors have been involved in drafting the manuscript and approved the final manuscript.

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Conflict of interest The authors declare that there are no conflicts of interests regarding the publication of this article.

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